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TRANSLATION

PROBLEMS IN DEVELOPMENT OF GLASS AND PORCELAIN INDUSTRY
(SELECTED ARTICLES)

FOREIGN TECHNOLOGY DIVISION

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PROBLEMS IN DEVELOPMENT OF GLASS AND PORCELAIN INDUSTRY (SELECTED ARTICLES)

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MICROCRYSTALLINE MATERIALS ON A GLASS BASE, THEIR PROPERTIES, AND FIELD OF APPLICATION

by

K. T. Bondarev

Microcrystalline materials on a glass base are obtained by means of their complete crystallization. They have better properties than original glass--greater mechanical strength, better heat resistance, higher softening temperature, and greater hardness.

The production of microcrystalline materials from glass by means of fusion of natural minerals, or their mixtures, with subsequent crystallization of the articles--"stoneware casting"--has been known for a long time. The production of synthetic microcrystalline materials from glass began to be developed comparatively recently. However, it has already attained considerable development.

Microcrystalline materials from glass in the USSR came to be called "sitalls" and in the USA "pyroceram." The "sitalls" generally are opaque, although in recent times transparent materials have been obtained.

According to Tamman [1] the process of crystallization is characterized by the rapidity of the growth of crystals and the rapidity of the formation of centers of crystallization. The problem of the original stage of the formation of crystalline nuclei up to now has remained unsolved [2].

In the opinion of Kuznetsov [2] the formation of nuclei of crystals in a supercooled liquid (glass) occurs in the following form. In fusion the molecules are in constant thermal motion. With the lowering of the temperature the kinetic and potential energy of the molecules diminishes. The molecules of the liquid, which have kinetic energy that is considerable as

compared with the molecules of the crystal, cannot form a stable aggregate, and each random accumulation of molecules which has formed as a result of the thermal motion rapidly decomposes. With the lowering of the temperature and consequently with the diminishing of the kinetic energy of the molecules, the accumulations of molecules which have been formed become more stable. Therefore at some temperature the appearance of crystalline nuclei becomes possible.

With the lowering of the temperature of the supercooling of the liquid (glass) the forces of friction increase, the movement of the molecules slows down, and the formation of nuclei of crystals is made more difficult, but the nuclei of crystals formed have greater stability and cease to decompose into separate molecules. If this takes place in the absence of extraneous particles the process is called homogeneous formation of centers of crystallization. If, however, the centers of crystallization of the new phase are formed on the surface of materials the chemical composition of which is different from the chemical composition of the new phase there occurs the process of heterogeneous crystallization, or the process of the formation of crystals in the presence of catalysts. The process of homogeneous formation of centers of crystallization in glasses is made difficult mainly from the extremely slow rate of formation of nuclei [3]. However, it is known that almost any glass can crystallize on the introduction into its composition of a small amount of catalysts.

In the cooling of glass which contains a catalyst down to a certain temperature, from the particles of the catalyst there are homogeneously formed nuclei of crystals which are produced spontaneously in submicroscopic form. After repeated heating at a certain temperature in the course of a certain period of time around the centers of crystallization formed there occur

heterogeneous formation and growth of crystals of the main components of the glass.

The process of the formation of centers of crystalliation also can be induced, as is the case in light-sensitive glasses, by means of effects on the cooled glass through short-wave (X-ray or ultraviolet) radiation.

A quantum of light, in interacting with the glass, either excites an ion of silver, gold, or copper (reaction a), or ionizes it (reaction b) with the formation of a free electron

$$Ag + h\nu \nearrow (Ag^{+})^{*} \quad (a)$$
$$Ag + h\nu \searrow Ag^{++} + e^{-} \quad (b)$$

In the process of heat treatment glass the electrons, knocked out by the quantum of active radiation, neutralize the ion of silver in accordance with the reaction

$$Ag^{+} + e^{-} \rightarrow Ag^{\circ} + h\nu_1; \quad \nu_1 < \nu. \quad (c)$$

The neutral atoms of silver associate and form centers of crystallization.

The catalysts of crystallization should be dissolved well in the glass at boiling and processing temperatures, and dissolved badly at lower temperatures. The catalyst should have great free energy of activation of the homogeneous formation of nuclei of cristals from the fused mass at low temperatures. The ions or atoms of the catalyst should diffuse in the glass at low temperatures more rapidly that the main components of the glass. For obtaining an effective steeping the int rsurface energy between the glass and the crystals of the catalyst should be small. And finally, the crystal structure and parameters of the lattice of the catalyst crystals and of the nuclei of the crystalline phase should be as close to each other as possible.

According to the researches by Mauer [4] the minimum size of a crystal

of gold capable of catalysing the crystallization of lithium silicate in light-sensitive glasses amounts to 80 Å (about 10,000 atoms). According to the data of Stukie [3] in crystallization there are formed from 10^9 to 10^{15} crystals for 1 mm^3 of glass. With simultaneous formation and growth of such a number of crystals there is assured full crystallization of the glass.

As a catalyst one uses fluorine, light-sensitive admixtures (gold. silver, copper) titanium oxide, platinum, oxide of phosphorus, iron and magnesium sulfides, etc.

At the present time the obtaining of microcrystalline materials on a glass base is being done in four basic directions. As a catalyst of the crystallization one uses fluorine, light-sensitive admixtures (gold, silver, copper), titanium oxide, and iron and manganese sulfide.

Microcrystalline Materials on a Base of Fluorine Glasses These were first obtained in 1954 in the Scientific-Research Institute of Construction Materials in Rumania. In 1956 analogous material was obtained in the experimental shop of the Avtosteklo Factory. In Rumania this material was designated as "porcelain from glass" and in the USSR as "glass porcelain."

The chemical composition of the glasses which are the base for obtaining glass porcelain correspond to the system SiO_2--Al_2O_3--MgO--CaO with the admixture of a small amount of alkali as fusing agent and fluorine as catalyst of the crystallization.

Glasses of this system should crystallize with high viscosity (minimum 10^{10}—10^{11} poise), which excludes deformation in the process of crystallization.

It has been established [5] that in the given case there occurs a heterogeneous crystallization of silicates on crystals of fluorides, brought

about, apparently, by the closeness of the constants of their crystalline lattices, and especially by the equality of the ion radii of oxygen and fluorine.

For obtaining glass porcelain one uses glass of the following chemical composition : SiO_2--55--58, Al_2O_3--14--18, MgO--7--10, CaO--12--15, Na_2O--5--6, and fluorine--5--7% (above 100%).

For introducing the fluorine into the glasses one can use fluorspar, fluosilicate of sodium, or cryolite. The temperature of boiling and clarification of the glass is 1,450--1,470°. After shaping the article it is submitted to firing, and afterwards to crystallization. The process of firing and crystallization can be combined and accomplished in one aggregate. The difficulty of the process of crystallization consists in the fact that original glass has a softening temperature of 550--650°, and the crystallization takes place in a temperature interval of 750--900°.

For preventing deformation of the articles in crystallization one uses the graduated curve of crystallization (curve 1, Fig. 1), which allows one to crystallize an article without change in its form. The essence of this process consists in the fact that in keeping the glass in the first stage there are formed in it crystals which reinforce the mass of glass, and this makes it more stable as against deformation in heating. In the second stage there occurs the full crystallization of the glass.

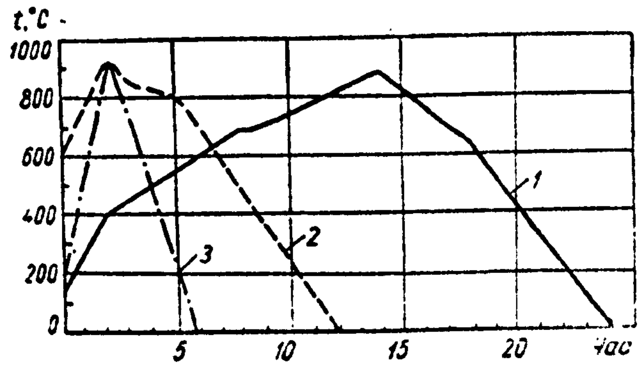

Fig.1 Temperature curve of crystallization of glass porcelain of the composition 00253

The procedure according to curve 2 enables one to obtain glass porcelain of the composition 00253 with the very best properties.

Individual articles less subject to deformation b cause of their special form and dimensions can go through the crystallization process according

Table 1

Designation of properties	Original glass for glass porcelain 00253	Glass porcelain 00253
Coefficient of linear expansion X 10^{-7} at 100--800°	70	88
Bending strength, kg/cm^2	350--400	800--1200
Impact strength	1	4
Heat stability, °C	40	250--300
Temperature of softening, °C	500--550	900
Microhardness under load load 100g, kg/mm^2	--	752

to curve 3 with a minimum of expenditure of time in the crystallization. The keeping of the glass at a temperature of 900° during the course of 10 to 15 minutes is sufficient for full crystallization of the whole mass, even in the case where the thickness of the walls of the articles is 30 mm.

The glass porcelain of the Avtosteklo Factory of the composition 00253 has a uniform fine-crystal structure (Fig. 2). In Fig. 3 there is shown an X-ray photograph of the same composition of glass porcelain taken in the structure laboratory of the Avtosteklo Factory.

Glass porcelain and articles made of it possess high mechanical strength and heat stability. Comparative data of the properties of the original glass and glass porcelain of the composition 00253 produced by the Avtosteklo Factory are shown in Table 1.

Of all the known microcrystalline materials glass porcelain proves to be the cheapest. It can be made from abundant raw material. Out of glass por e-

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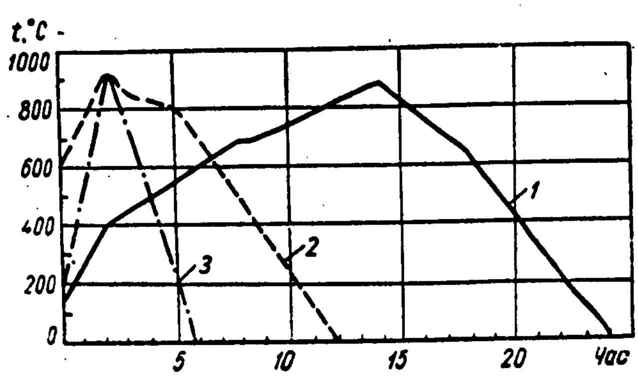

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lain one can make floor slabs, wall panels and slabs, stairsteps, window sills, partitions, roofing materials and other things. Articles made of glass porcelain have a frosty-white color, and they maay be colored over the whole mass or be streaked, as in the case of marble. Since it has high r mechanical strength and better dielectric properties than porcelain, glass porcelain is worth considering when it comes to making all types of insulators, especially such as require high mechanical strength.

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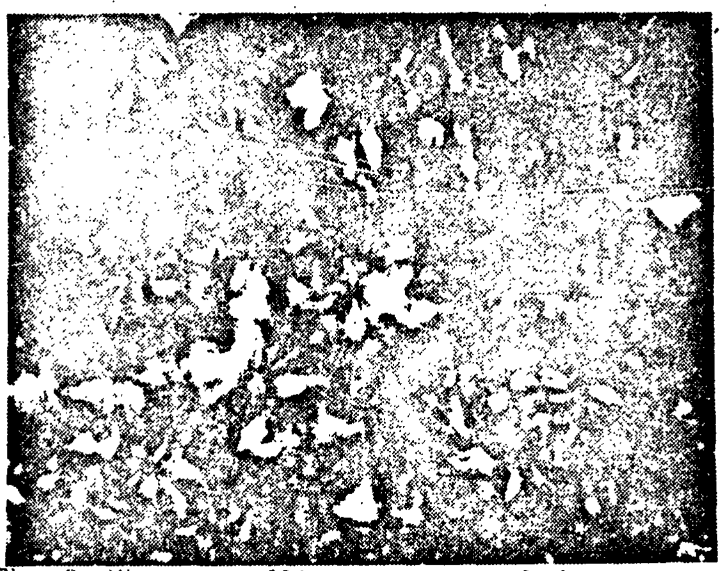

Fig. 2. Microcrystalline structure of glass porcelain of the composition 00253 (X 300)

Comparative date of the properties of insulators made of glass porcelain of the composition 00253 and of porcelain of the the Slavyansk Insulator Factory are given in Table 2.

The use of glass porcelain for making insulators makes it possible to automate the process of production. Out of glass porcelain it is possible to make tubes that are heat-resistant and resist the action of chemicals as well as vessels for everyday and laboratory use and parts of machines subject to attrition and which work in corrosive media and at high temperatures. Glass porcelain is suitable for making press forms, used for molding plastics under pressure, low-melting metals, etc.

<u>"Sitalls" on the Base of Light-Sensitive Glasses</u> These represent fine-crystal materials on the base of glasses of the system Li_2O--Al_2O_3--SiO_2,

which give after crystallization the minerals: β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$), β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$), disilicate and metasilicate of lithium, or a solid solution of these minerals. As catalysts of the crystallization one uses insignificant additions of gold, silver, or copper.

The founding of the glass is done at temperatures of 1470 to 1550°. Articles are formed by casting, pressing, blowing, centrifugal casting, etc.

(See page 8a for fig. 3)

Fig. 3. X-ray analysis of glass porclain of the composition 00253

AC2S--anorthite; NAGS--albite; CM2S--diopside; MS--enstatite

After firing the articles are subjected to the action of ultraviolet or X-rays. In the process of radiating around the atoms of silver, gold or copper there are formed submicroscopic centers of crystallization. The radiated glass undergoes crystallization at 800 to 1150°.

T a b l e 2

Property	Units of Measurement	Technical Requirements	Indices: Glass porcelain	Indices: Porcelain
Dry-discharge voltage	kv	60	62--65	60--64
Microdischarge "	kv	34	35--36	35--37
Puncture "	kv	78	80--85	83--85
Breakdown load	kv	1400	4600--5900	1800--2500

The properties of crystalline materials prepared in the USA are given

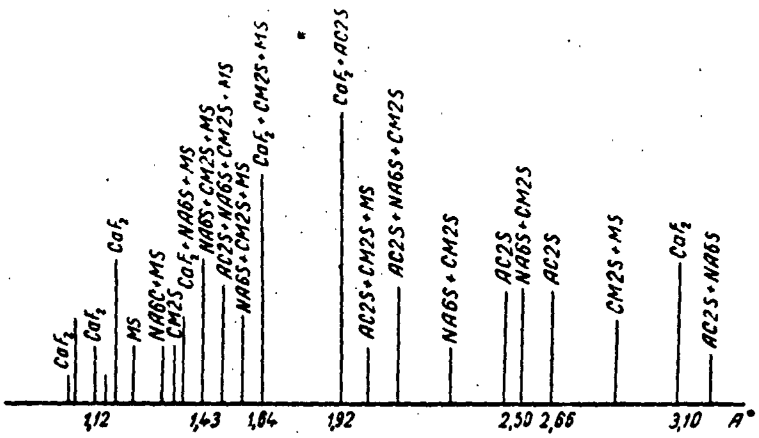
CaF2
CaF2
CaF2
MS
NA6C+MS
CM2S
CaF2+NA6S+MS
NA6S+CM2S+MS
AC2S+NA6S+CM2S+MS
NA6S+CM2S+MS
CaF2+CM2S+MS
CaF2+AC2S
AC2S+CM2S+MS
AC2S+NA6S+CM2S
NA6S+CM2S
AC2S
NA6S+CM2S
AC2S
CM2S+MS
CaF2
AC2S+NA6S
1,12
1,43
1,84
1,92
2,50
2,66
3,10
A°

Fig. 3

in Table 3.

Table 3

Designation of properties	Pyroceram 9606 of Corning Company, U. S. A.	Pyroceram 9608 of same company
Specific weight at 25°	2.60	2.50
Temperature of softening, °C	1250	1250
Coefficient of Linear expansion, X 10^{-7}	57	7
Dielectric constant at frequency 10^{10} cps:		
at 25°	5.45	6.71
" 300°	5.51	--
" 500°	5.53	--
Coefficient of dielectric losses at frequency 10^{10} cps:		
at 25°	0.00033	--
" 300°	0.00075	--
" 500°	0.00152	--
Resistance to breakdown, kg/cm^2	1400	1100--1600

On a base of light-sensitive glasses there were obtained there were obtained "sitalls." The use of the light-sensitive glasses makes it possible to obtain photographic images. Relief images are obtained by means of etching in fluoric acid light-sensitive glass after radiating by Y-rays or ultraviolet rays and heat treatment. When this is done the crystallized part etches away faster than the basic glass.

The "photosital" is used widely in printing systems and typographic cliches, in radio electronics, in the form of micromodule plates and complicated forms with openings, for microphotography of valuable books and drawings which have to be preserved a long time without damage, for producing plates with a

a great number of holes (5--10 thousand holes per cm^2), for making parts in color television, etc.

"<u>Sitalls</u>" <u>with a Catalyst in the Form of Titanium Oxide</u>. The "Sitalls" or pyrocerams in which the centers of crystallization are formed with the aid of titanium oxide represent microcrystalline materials obtained on the basis of glasses of the following systems:

$$Li_2O—Al_2O_3—SiO_2$$

$$MgO—Al_2O_3—SiO_2$$

$$CaO—MgO—Al_2O_3—SiO_2$$

The lithium-aluminum-silicate compositions after crystallization give β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) and βeucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) or their solid solutions.

These compositions find application for making microcrystalline materials with a low expansion factor.

The magnesium-aluminum compositions after crystallization give mainly solid solutions of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) and rutile (iO_2).

Pyrocerams on the base of magnesium-aluminum-silicate compositions prove to be cheap and to have very good prospects. They have greater mechanical strength, high-temperature stability, and good radio-technical properties.

Pyrocerams on a cordierite base have already found application and will be used more widely in construction ~~work, radio~~ electronics, electrical engineering, and machine building.

Literature Cited

1. G. Tamman, Glass-formation state, United Scientific and Technical Publishing Offices, 1935.

2. V. D. Kuznetsov, Crystals and crystallization, State Publishing Office, 1953.

3. Stukie, Theory and practice of catalytically excited crystallization in glass, Glastechn. Berichte (Glass Technology Reports), 32 (1959).

4. Mauer, Nucleus formation and growth of crystalls in light-sensitive glass, J. Appl. Physics, 29, 1 (1958).

5. Lungu and Popescu-Hoch, Masses from thin ceramics obtained by crystallization of glass (porcelain from glass), Industria Usoara, 2, 63, (1958)

HIGH-STRENGTH CERAMIC MATERIALS FOR HIGH-VOLTAGE INSULATORS

by

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In recent times at insulator factories that there have been tried out for the making of high-voltage insulators some new high-strength ceramic materials: zirconium (Ts-35), ascharite (B-44), and corundomullite (KM-1 and No. 133). The basic physicotechnical characteristics of these materials obtained by the Factory Proletariy [proletarian] and also of high-voltage phosphorus are given in Table 1. The materials Ts-35 and B-44 have not found application in industry due to their scarcity and the high cost of the raw material (material Ts-35), and also because of a number of technological difficulties (preparation of sintering, complications in firing in connection with the narrow interval of the sintered state for the material B-44, and others).

From the material KM-1, which is characterized by the highest mechanical strength at the Factory Proletariy there were prepared insulators for air switches carrying 500 kv with test pressure 90 and 80 kg/cm^2.

In view of the difference, both as to the charging and the granulometric composition of the mass KM-1 from high-voltage porcelain, the technology of the making of articles from it proved to be considerably more complicated than making them out of porcelain. In working with the material KM-1 it is necessary to observe very precisely all technological parameters.

The deviations in the processes of drawing, drying and firing of articles result in scrap conditions in the form of a crack (in the semimanufactured article), underfiring, and deformation in firing. Therefore the mass KM-1 has not found wide use for making large-dimensioned, high-voltage insulators.

Trying out in production has shown that the technology of making articles out of the mass No. 133 is fully the same as in making them from the usual porcelain mass. The scrap in drying and firing in this case is insignificant. The mechanical strength of the articles from mass No. 133 is 1.5 higher than that of articles of porcelain mass. Bracket insulators from the mass No. 133 break down under loads of 2,500 kg, and those of porcelain under loads of 1,500 kg. Insularors for air switches under 500 kv (factory No. IP-856) sustain a test pressure of 80 to 100 kg/cm^2. The material No. 133 now is being made use of by the Factory Proletariy for making a wide assortment of articles with high mechanical strength.

The Leningrad branch of the GINKI investigated a material with a higher quartz content and porcelain body, and with replacing them with fired kaolin and alumina, as well as with a more thinly ground mass (0.5% of residue in sieve No. 006). The results of this work are given in Table 2. They show that the mechanical strength increases with a decrease in the coarseness of the grinding, and with a residue of 0.5% on the sieve No. 006 it reaches 1,000 kg/cm^2. With the increase in the amount of quartz up to 38%, and of porcelain body up to 16%, the mechanical strength also increases up to 1,000 kg/cm^2. The introduction of alumina of the modification a (80 to 90%) enables one to increase the mechanical strength by 1.5 times as compared with high-voltage porcelain. The electrical strength remains at the level of the High-voltage porcelain and improves with the use of feldspar with a high ratio of K_2O, and with an increase in the fineness of the grinding.

In the process of the work there was solved the question of the industrial obtaining of alumina with a content a- Al_2O_3 of the order of 90% from the Volknov Aluminum Factory.

The Leningrad branch of the GIEKI (State Electric Ceramics Research Institute) developed a new material No. 133 with moderate mechanical strength in place of high-voltage porcelain for articles which bear a heavy mechanical load. The composition of the mass No. 133. The composition of the mass 133 is obtained by introducing into a high-voltage porcelain mass 18% of alumina at the expense of taking out porcelain body and part of the quartz.

Table 1

Characteristics	Material: High-voltage porcelain	B-44 (ascharite)	Ts-35 (zirconium)	KM-1 (corundo - mullite)	No. 133
Limit of strength in static bending kg/cm^2 (on specimens of the diameter of 10 mm)	700--850	1400--1500	1350--1400	1600--1800	1100--1200
Limit of strength in rupture, kg/cm^2	250--350	400--600	400--600	400--600	500
Limit of strength in impact bending kg/cm^2	1.7--2.5	2.4--2.7	1.8--2.5	2.4--2.7	3.2
Heat resistance °C (mean breakdown drop in temperature)	180	190	200	190	190
Dielectric loss-angle tangent at frequency 50 cps, 20°	0.035--0.045	0.0018--0.0040	0.025--0.033	0.003	--
Specific volumetric resistance (at 100°) ohm/cm	10^{14}	10^{14}	10^{14}	10^{14}	10^{14}
Breakdown voltage of electric field kv/mm effect	25--30	20--27	25	22--31	25--30
Optimum teperature of firing, °C	1280--1320	1310--1330	1320--1350	1300--1350	1300--1320

Table 2

Designation of mass	Best compositions of mass, %: Kaolin, millet sieve	Kaolin, kyschtymite	Clay, Chasov Yar	Quartz sand, Lyuherter	Pegmatite, Priladozhskiy	Breakage porcelain	Fired at 1350°: Kaolin	Fired at 1350°: Alumina	Coarseness of mass, residue on Sieve No. 006, %	At optimum temperature: Limit strength in static bend kg/cm²	Breakdown voltage kv/mm effect	Temperature of firing, °C	Module of elasticity, kg/cm². 10^{-6}
А-4	14	14	17	13	37	5	—	—	0,5%	1042	35,5	1300	0,73
Б-7	14	14	17	13	37	5	—	—	1,5%	950	29,9	1320	0,72
В-9б	14	14	17	—	37	—	18	—	1,5%	1178	23,2	1350	0,85
В-9в	14	14	17	—	31	—	24	—	1,5%	1206	24,1	1350	0,83
Г-12б	14	14	17	—	37	—	—	18	1,5%	1270	27,0	1320	0,95
Г-12	14	14	17	—	29*	5	—	21	1,5%	1455	30,8	1380	0,92
Д-14	14	14	17	10	29*	16	—	—	1,5%	1020	35,8	1320	0,74
Д-16	14	14	17	38,5	16,5**	—	—	—	1,5%	1051	28,9	1320	0,71

* In the composition Г - 12 and Д - 14 pegnatite enters in the form of 21% of feldspart and 8% of pegnatite.

** In the composition Д - 16 pegnatite enters in the form of 10.8% of feldspar and 5.7% of pegnatite.

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